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DTA STUDY OF THE INTERACTION OF S_2Cl_2 WITH IRON

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MICROMEDIA

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by

S.A. Mikhail

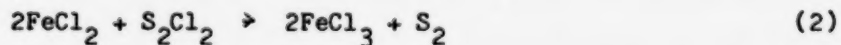
INTRODUCTION

A study of the interaction between sulphur monochloride, S_2Cl_2 , and iron powder was initiated on the request of V.M. McNamara, CANMET, as a first step towards a large scale investigation of the feasibility of the following reaction:



in the temperature range 350-450°C.

While reaction 1 is thermodynamically favourable at relatively low temperatures, kinetically several potential complications, such as coating of the particles with molten sulphur and the solubility of $FeCl_2$ and sulphur in S_2Cl_2 and consequently the diminishing of the S_2Cl_2 activity, may occur. Reaction 1 was investigated previously by Titi-Manyaka using thermogravimetry (1). He reported that metallic iron reacted with S_2Cl_2 rapidly at low temperature (<200°C) to form ferrous chloride and elemental sulphur. Further chlorination of ferrous chloride according to the following equation:



was suppressed in the presence of sulphur vapour. However, when tested independently, reaction 2 was reported to take place readily in the temperature range 200-350°C (1). By comparison, however, reaction 1 is thermodynamically much more favourable than reaction 2.

EXPERIMENTAL

Differential thermal analysis (DTA) was used in the present work as the main technique, with X-ray diffraction (XRD) and scanning electron microscopy (SEM) as supplementary techniques. Three types of iron powder were provided as starting materials; "Chesbar iron powder", "iron metal powder (electrolytic)", and "iron metal filings (fine)". XRD analysis indicated minor impurities such as wustite, quartz and siderite in the last two types and no impurities in the Chesbar iron powder. Practical grade sulphur monochloride from Eastman Kodak Company, Rochester, N.Y., U.S.A. was used.

A schematic diagram of the DTA equipment, with a specially designed arrangement for the introduction of S_2Cl_2 , used in the present study is shown in Figure 1. A quartz sample holder and a refractory block were employed. Calcined alumina was used as a reference material. A variable-speed syringe pump (Sage Instruments, Model 220), was used to inject liquid sulphur monochloride at a constant rate of 1.5 mL/min through a glass capillary which extended into the hot zone of the tube furnace. An outer tube around the capillary was used to introduce the argon gas which mixed with the sulphur monochloride vapour before entering into the reaction zone through entrance 13. The total argon flow rate was 100 mL/min, of which about 5% was entered through entrance 12 to minimize back diffusion and condensation of S_2Cl_2 at the colder part of the reaction tube. At the exit side of the reaction tube, a heating tape was used to prevent S_2Cl_2 condensation.

The iron powders were ground and screened to two selected particle sizes, namely -200+325 mesh (44-74 μm) and -325 mesh (44 μm). A sample weight of about 20 mg was chosen. The samples were heated in the DTA Assembly (heating rate 10°C/min) under argon flow up to the desired temperature at which sulphur monochloride was injected. When the desired upper temperature limit was reached, heating was discontinued and the S_2Cl_2 flow was stopped while the argon flow was maintained until the system cooled down to ambient temperature. The reaction product was examined under the microscope, by X-ray diffraction and by the back-scattered electron (BSE) facility of the scanning electron microscope. The latter technique, which is only slightly affected by surface irregularities, was chosen because of the difficulties encountered

in producing a smooth surface polished section due to the hygroscopic nature of the reaction product, and hence the inability to use the electron microprobe facility. Qualitative energy dispersive X-ray analysis (EDXA) was conducted with the SEM to show the elemental distribution of iron, chlorine and sulphur in the reaction product.

RESULTS AND DISCUSSION

In spite of the different degrees of purity of the three types of iron powders examined by DTA, no major differences were noticed in their chlorination behaviour. Only minor differences were observed in the behaviour of samples with the two different particle sizes. The samples were subjected to chlorination in the temperature range 350°-450°C in most experiments and in the temperature range 300-500°C in a few experiments.

The DTA results of the chlorination of all examined iron samples indicated that a highly exothermic reaction took place as soon as S_2Cl_2 reached the sample. A large exothermic peak commenced very sharply on the DTA diagram and was followed by a slow exothermic trend up to the end of the experiment at 450 or 500°C. Microscopic examination of the product indicated the presence of beige and greenish materials, which were soluble in water, together with black unreacted particles.

X-ray diffraction analysis indicated that the product consisted of iron metal and ferrous chloride. No iron sulphide was detected (XRD, however, may not detect components of less than 5% in the examined sample). However, a sensitive analytical test for sulphides (2), in which traces of the sulphide act as a catalyst for iodine-azide reaction, was performed on the product and the result was found positive.

By examining the BSE and X-ray micrographs of the product, Fig. 2, it can be seen that, in spite of the strong reaction indicated by DTA, the starting iron particles were not entirely consumed by the reaction. In Figure 2a, the unreacted iron cores are shown surrounded by reaction products. In Figures 2b, c and d, X-ray mapping of iron, chlorine and sulphur, respectively, indicated that Fe-Cl and Fe-S compounds and possibly elemental sulphur are distributed in the product layer around the iron core. It is also evident

that the amount of sulphur is small compared with the chloride in the product.

The results of the present work are consistent with the following mechanism. After the initial reaction between S_2Cl_2 and the iron particles, a product layer forms around each particle and further reaction may take place by diffusion of the gas through the product layer to interact with the iron core at the solid-solid interface according to reaction 1. A concentration gradient of S_2Cl_2 is established through the product layer with lower concentrations nearer to the core-product interface. The sulphur, produced by reaction 1, also establishes a concentration gradient with the highest concentration at the core product interface and the lowest concentration at the solid-gas interface where sulphur volatilizes quickly in the gas stream (the vapour pressure of sulphur at 600 K (327°C) is 16 kPa (120 Torr)). The sulphur activity is, therefore, at its maximum at the core product interface which may account for the formation of iron sulphide in this region.

CONCLUSION

DTA equipment with a specially designed system to handle S_2Cl_2 flow was assembled for the present work. The study of the interaction between S_2Cl_2 and iron indicated that the reaction takes place at relatively low temperatures (300°C) with the formation of ferrous chloride and to a much smaller extent iron sulphide. The formation and build up of a product layer around the unreacted core delayed the completion of the reaction by separating the reacting species.

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REFERENCES

1. Titi-Manyaka, R. and Iwasaki, I. "Chlorination behaviours of complex iron, copper and nickel sulphides"; Trans Soc Min Eng - AIME 260:282-288; 1976.
2. Feigl, F. "Spot tests in inorganic analysis" 5th ed., Publ. Elsevier Publishing Co., New York, page 305; 1958.

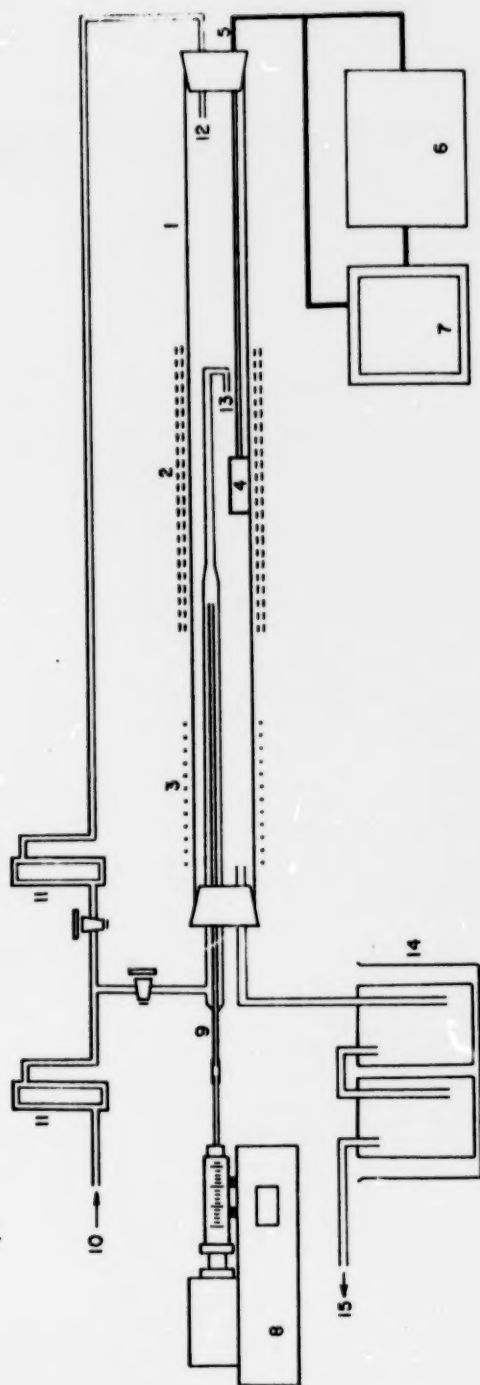


Fig. 1: DTA assembly for S_2Cl_2 atmosphere.

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|---------------------------|--|
| 1. Reaction tube. | 8. Variable-speed syringe pump. |
| 2. Tube furnace. | 9. Capillary (1 mm i.d.) for S_2Cl_2 delivery. |
| 3. Heating tape. | 10. Argon gas. |
| 4. DTA block. | 11. Flowmeter. |
| 5. Thermocouple assembly. | 12. Inlet for argon. |
| 6. Millivolt amplifier. | 13. Inlet for S_2Cl_2 -Ar mixture. |
| 7. Strip chart recorder. | 14. Ice bath. |
| | 15. Gas outlet. |

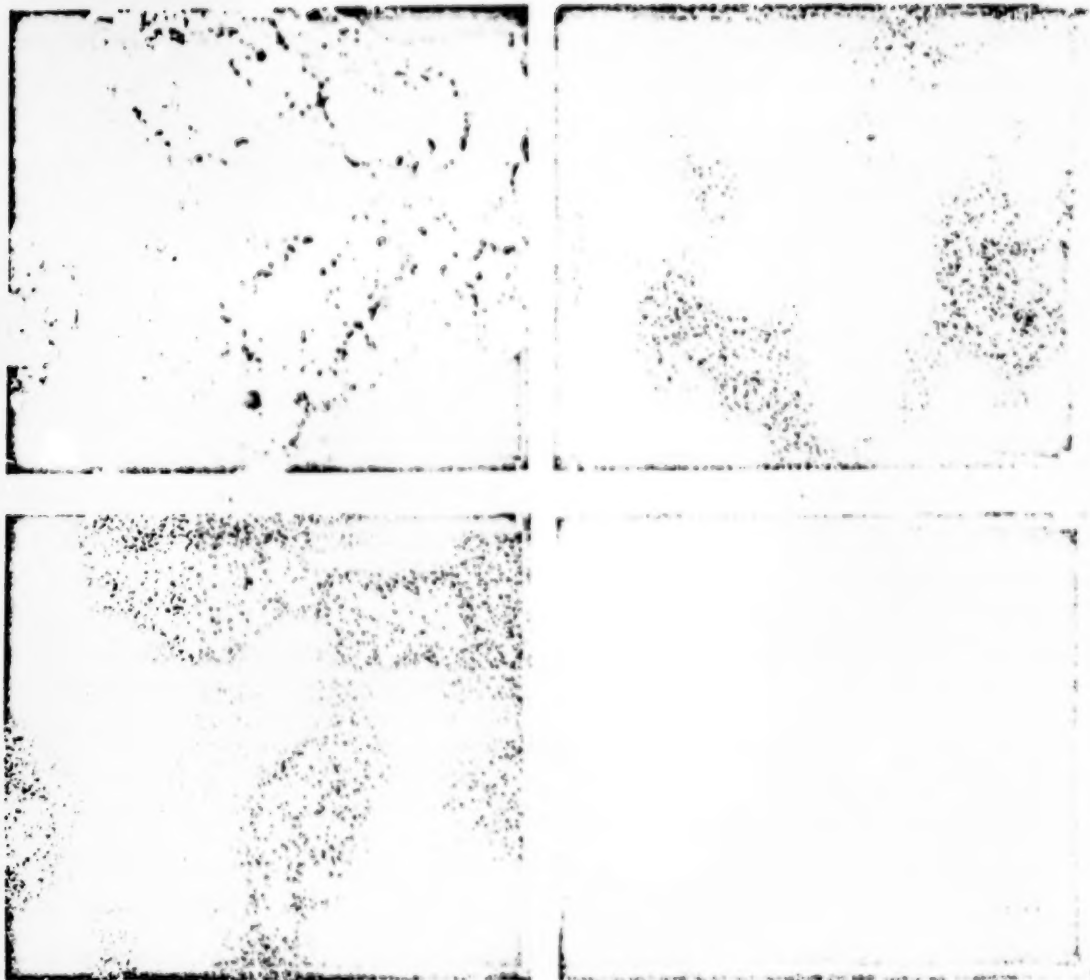


Fig. 2: BSE- and X-ray micrographs of chlorinated iron powder (electrolytic)

- a. BSE micrograph showing unreacted iron (white) in a matrix of FeCl_2 .
- b. X-ray micrograph showing the distribution of iron in a.
- c. X-ray micrograph showing the distribution of chlorine (as chloride) in a.
- d. X-ray micrograph showing the distribution of sulphur (as Sulphide) in a.

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